

Research in New Ionic Liquids

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14. ABSTRACT LiquidsIonic Liquids are a family of salts which by definition have very low melting points that are at or below the boiling point of water (<100°C).1-4 They typically have very long liquidousranges before they decompose, with essentially no vapor pressure in theirliquid state and have found a special niche in the field of chemistry.Work in the last decade has experienced exponential growth with efforin applications of ionic liquids as novel solvents for a wide range of reactions. However,efforts in the area have been going on for several decades and most notably those bythe USAF. L. King, J. Wilkes, and C. Hussey began pioneering efforts with this unusualclass of materials in the 1960Ÿs with applications centered uponfinding new electromilitary batteries.5This work centered heavily upon diN,NŸ alkyl substitutedimidazoliumsalts most of which were water sensitive due to the anion. Thislong lived efforfinally resulted in the discovery of water stable systems in theearly 1990Ÿs opening the doormany applications.6Since that time, much of the effort has centered upon the use of ionic liquids as excellent reaction solvents, extraction media, and as catalyst carriers. Unfortunately, little efforhas centered upon the basic scientific question of why these salts are low melting and how othersystems might be discovered. We have focused our research efforts on the design, synthesis and characterization of new families of ionic liquids using new heterocyclic platformunderutilized anions, in finding new families of salts.		
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Those involved in this work



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Synthesis and
Characterization



Greg Kaplan
Synthesis and
Characterization



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Theoretical
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crystallography



Tommy Hawkins
6.2 Effort



Joann Larue
Synthesis and
Characterization



Background of Ionic Liquids

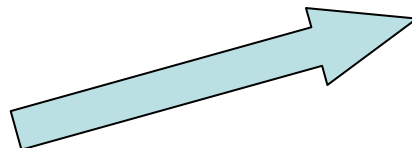
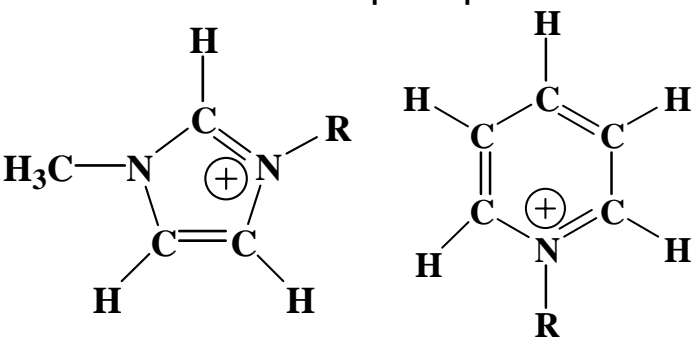
Ionic Liquids are a family of salts which by definition have very low melting points that are at or below the boiling point of water ($\leq 100^{\circ}\text{C}$).¹⁻⁴ They typically have very long liquidous ranges before they decompose, with essentially no vapor pressure in their liquid state and have found a special niche in the field of chemistry.

Work in the last decade has experienced exponential growth with efforts mainly in applications of ionic liquids as novel solvents for a wide range of reactions. However, efforts in the area have been going on for several decades and most notably those by the USAF. L. King, J. Wilkes, and C. Hussey began pioneering efforts with this unusual class of materials in the 1960's with applications centered upon finding new electrolytes for military batteries.⁵ This work centered heavily upon di N,N' alkyl substituted imidazolium salts most of which were water sensitive due to the anion. This long lived effort finally resulted in the discovery of water stable systems in the early 1990's opening the door for many applications.⁶ Since that time, much of the effort has centered upon the use of ionic liquids as excellent reaction solvents, extraction media, and as catalyst carriers. Unfortunately, little effort has centered upon the basic scientific question of why these salts are low melting and how other systems might be discovered. We have focused our research efforts on the design, synthesis and characterization of new families of ionic liquids using new heterocyclic platforms, as well as underutilized anions, in finding new families of salts.



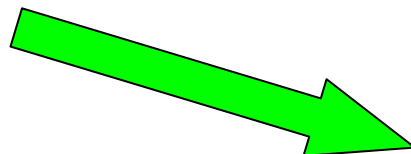
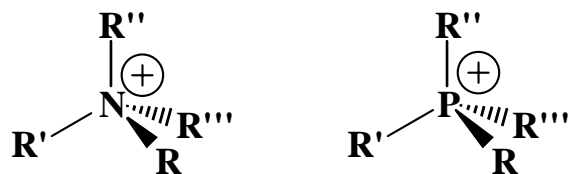
Current Efforts in the Area of Ionic Liquids

State of the art ionic liquids include N-alkyl-substituted imidazolium, pyridinium, tetraalkylammonium and phosphonium cations paired with a wide array of anions.



Hydrophilic Salts

Include cations with short alkyl groups such as ethyl and propyl with anions such as halides, acetates, nitrates, tetrafluoroborates, and perchlorates



Hydrophobic Salts

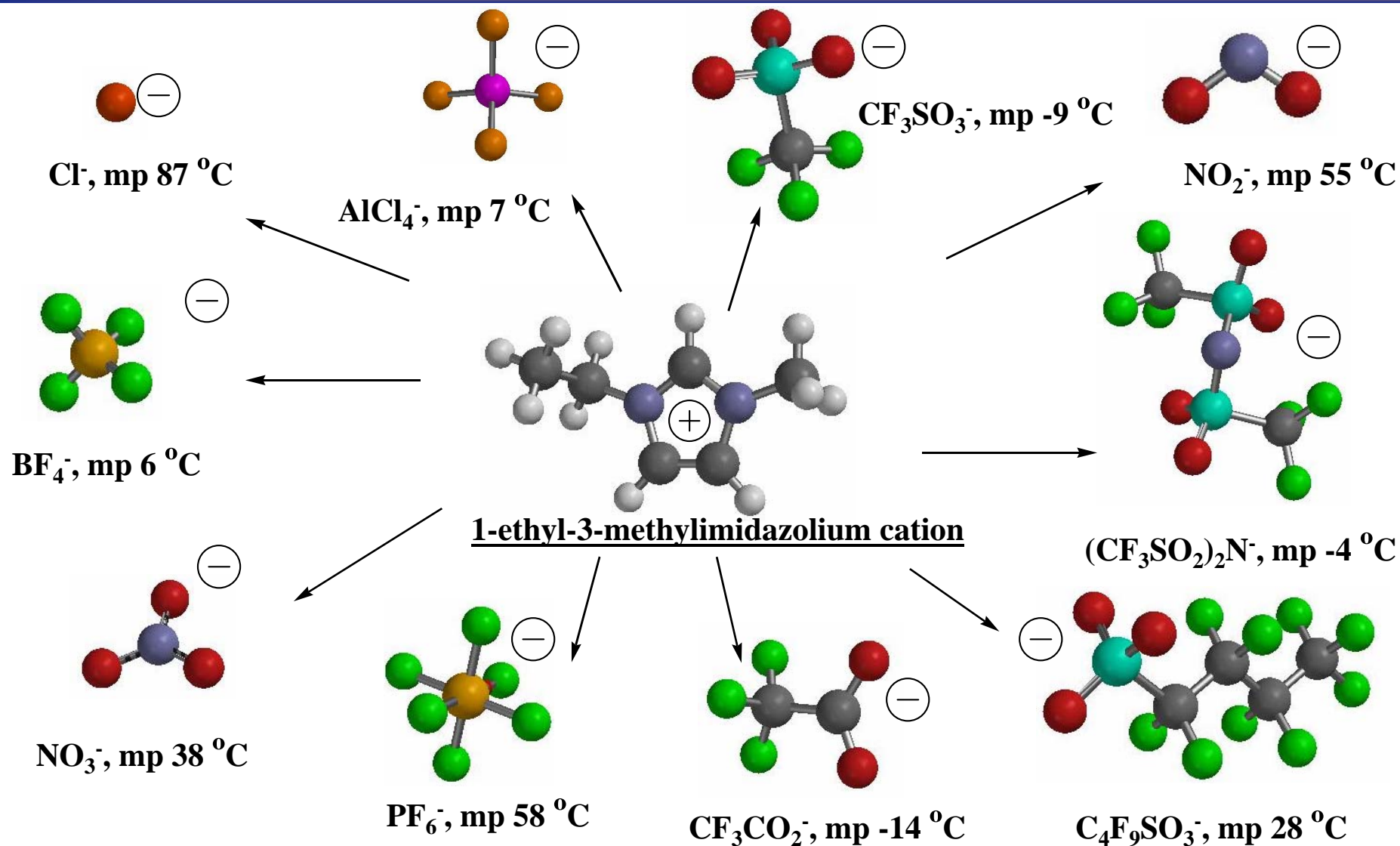
Include cations with long alkyl groups such as butyl and hexyl with anions such as tetraalkylborates and bistrifluoromethylsulfonamide.

Cation Families

Based on the length of the alkyl chains upon the cation as well as the nature of anion, ionic liquids have a wide array of physical properties including large changes in polarity, density, viscosity, and hydrophobicity/hydrophilicity behavior. This gives chemists many possibilities of various ionic liquid combinations for their specific reaction needs. Many of these are now commercially available from small research scale to multi-ton quantities. Commercial vendors include QUILL, Solvent Innovation, Merck, Cytec, and Sachem for these families of materials.



Effect on Melting Point with Various Anions

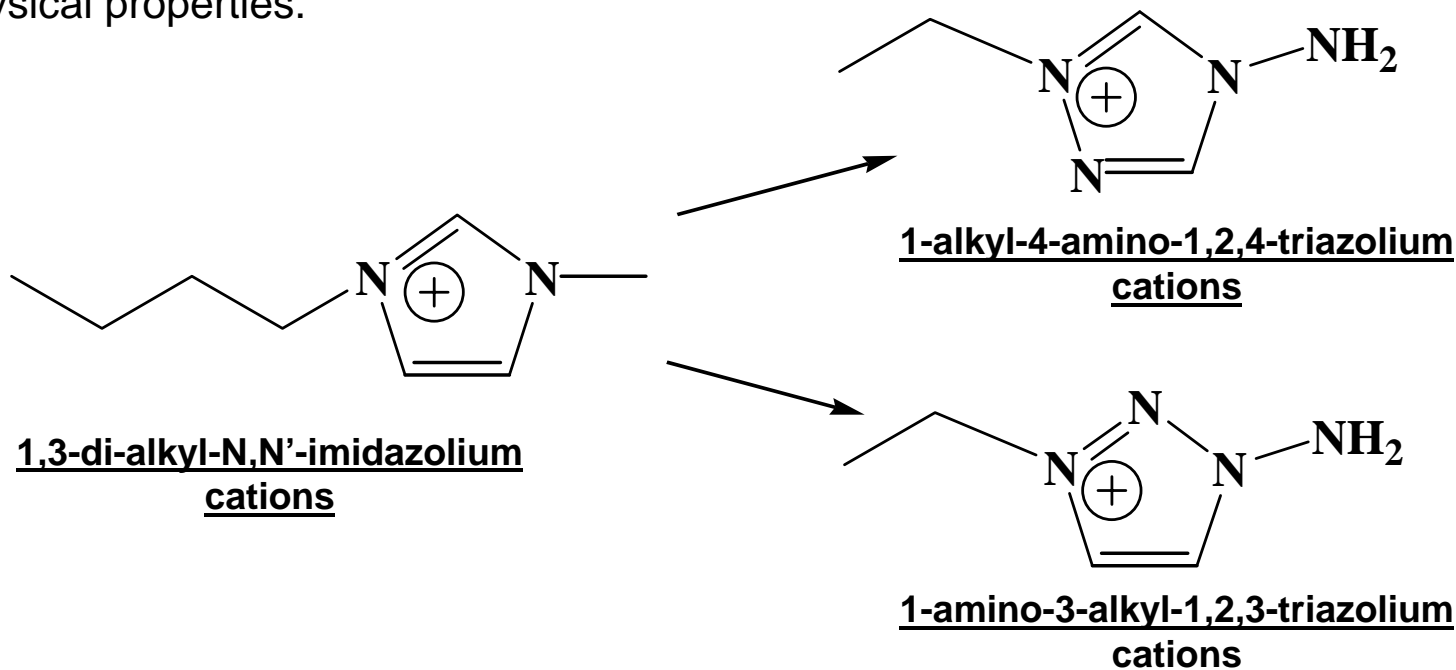




Research Efforts at AFRL



At AFRL, we are designing new classes of ionic liquids having the desirable physical properties of a low melting point and a reasonable liquidous range as the well known imidazole ionic liquids. We are using a methodology based upon pairing highly asymmetric cations with delocalized charged oxyanions. Heteroatom substitution in five-membered heterocyclic rings strongly affects physical properties such as melting point, viscosity, and decomposition onset. Specifically, the use of N-amino substituted heterocycles (4-amino-1,2,4-triazole and 1-amino-1,2,3-triazole) as building platforms has been extremely rewarding with the discovery of new classes of ionic liquids. Simple N-alkylation reactions have resulted in two new large families of ionic liquids with similar shapes as their imidazolium based analogs, with interesting effects on their physical properties.

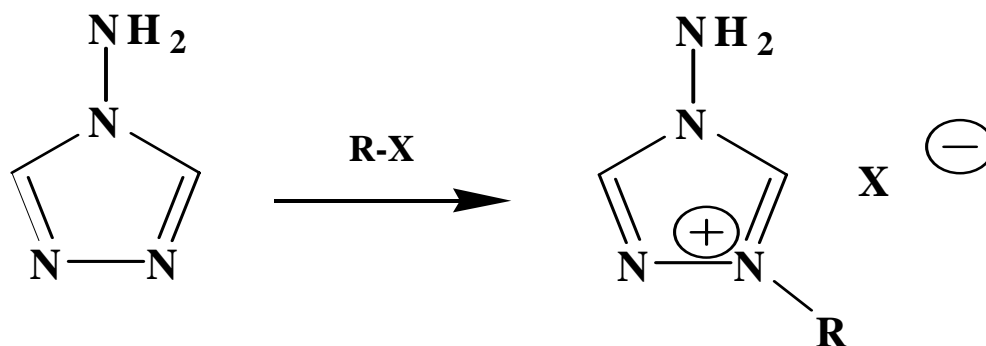




Work with 1-Alkyl-4-Amino-1,2,4-Triazolium Salts



Using a previously reported synthesis route⁷, we expanded and improved the procedure to make a large family of 1-substituted-4-amino-1,2,4-triazolium halide salts in high yield and purity⁸. These halide salts meet the well accepted definition of an ionic liquid¹⁻⁵ with all having mp <100°C.

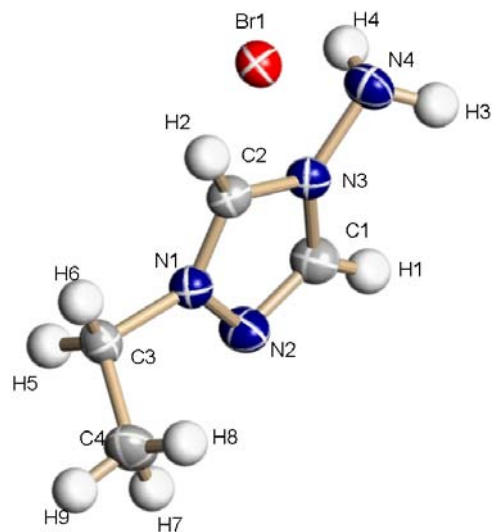


Substituted 4AT salts	m.p. (°C)	dec. onset (°C)	density (g/cm ³)
1-ethyl	63	110	1.69
1-n-propyl	60	120	1.56
1-isopropyl	90	110	1.60
1-butyl	48	130	1.46
1-n-pentyl	54	130	1.37
1-n-hexyl	76	120	1.34
1-n-heptyl	94	120	1.30
1-n-octyl	80	135	1.27
1-n-nonyl	81	140	1.26
1-n-decyl	90	135	1.23

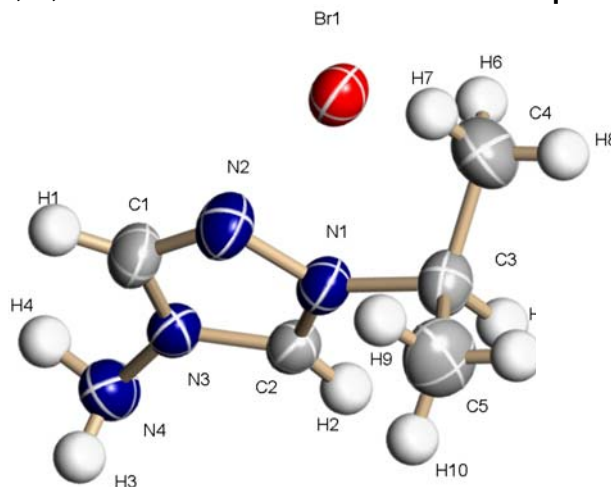


X-ray Structures of Ionic Liquids

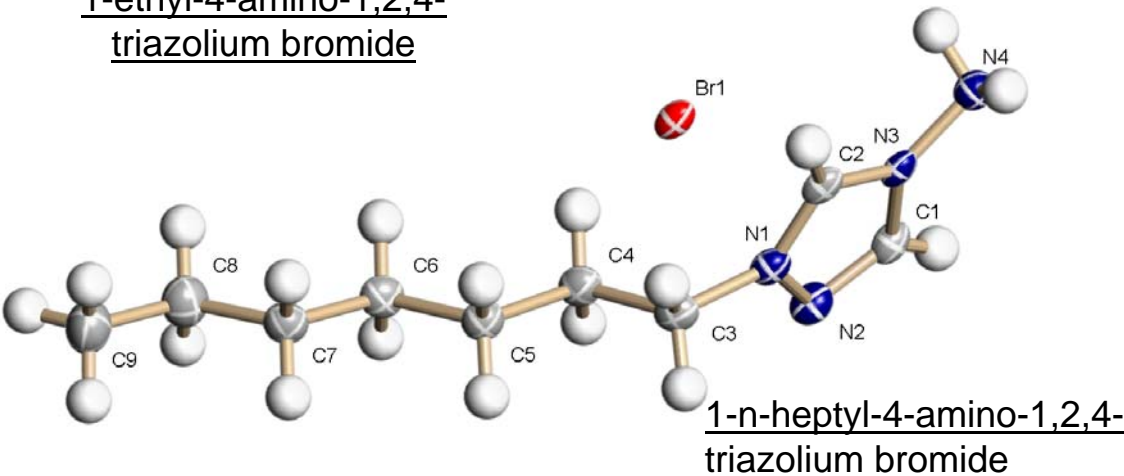
Single crystal x-ray diffraction studies carried out at Edwards AFB have verified the structures of several new 1-substituted-4-amino-1,2,4-triazolium halide ionic liquids.⁸



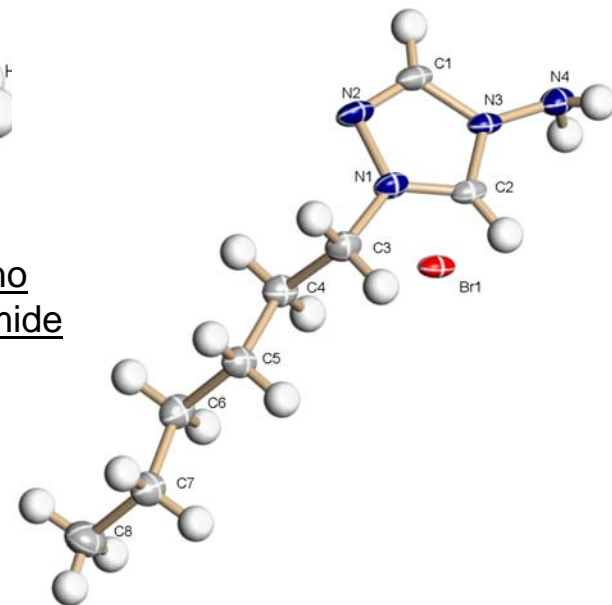
1-ethyl-4-amino-1,2,4-triazolium bromide



1-isopropyl-4-amino-1,2,4-triazolium bromide



1-n-heptyl-4-amino-1,2,4-triazolium bromide

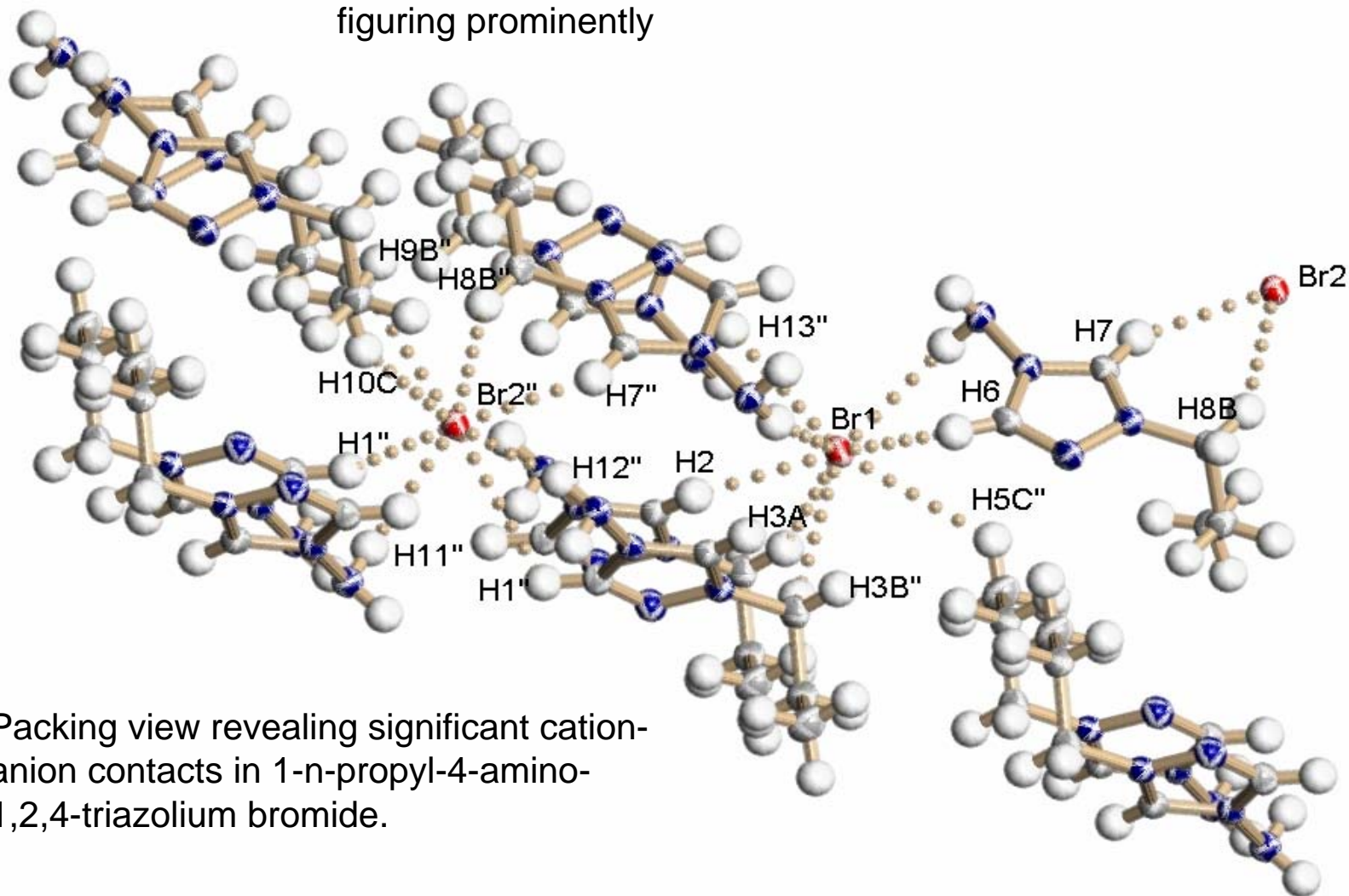


1-n-hexyl-4-amino-1,2,4-triazolium bromide



X-ray Analysis Reveals Extensive Hydrogen Bonding

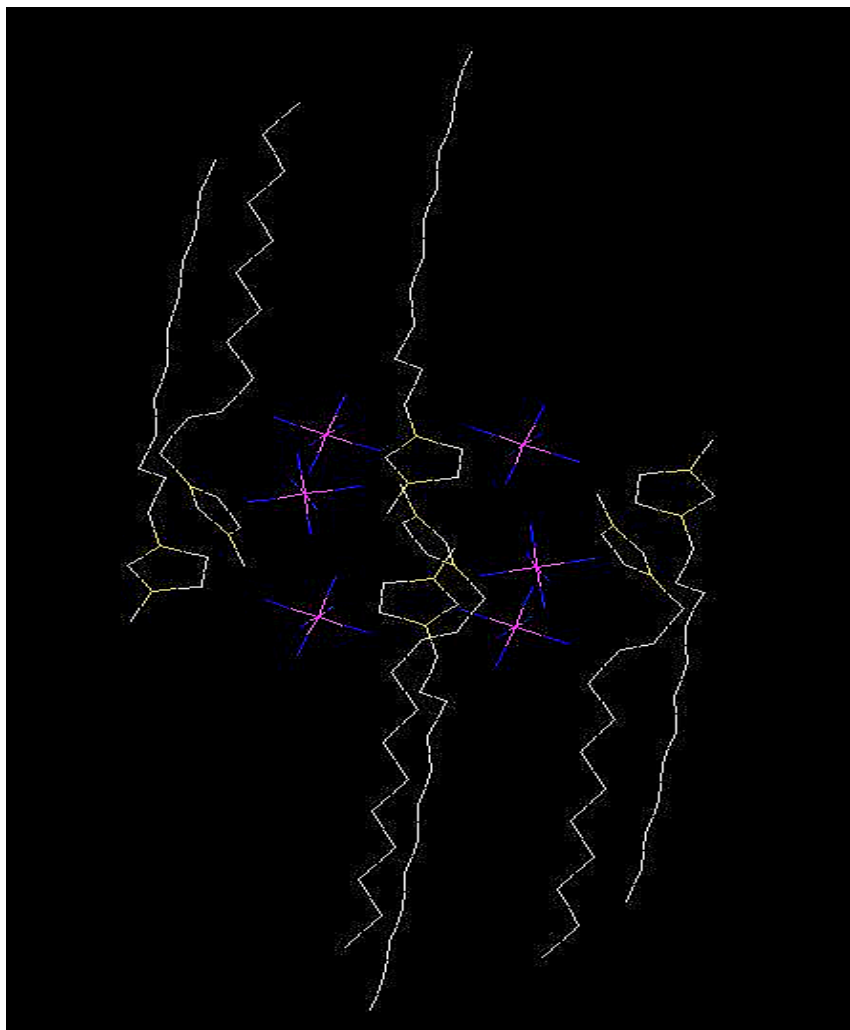
Extensive hydrogen bonding dominates the solid state packing of all 1-alkyl-4-amino-1,2,4-triazolium salts, with interactions of the halide with the N-amino protons of the heterocycle figuring prominently



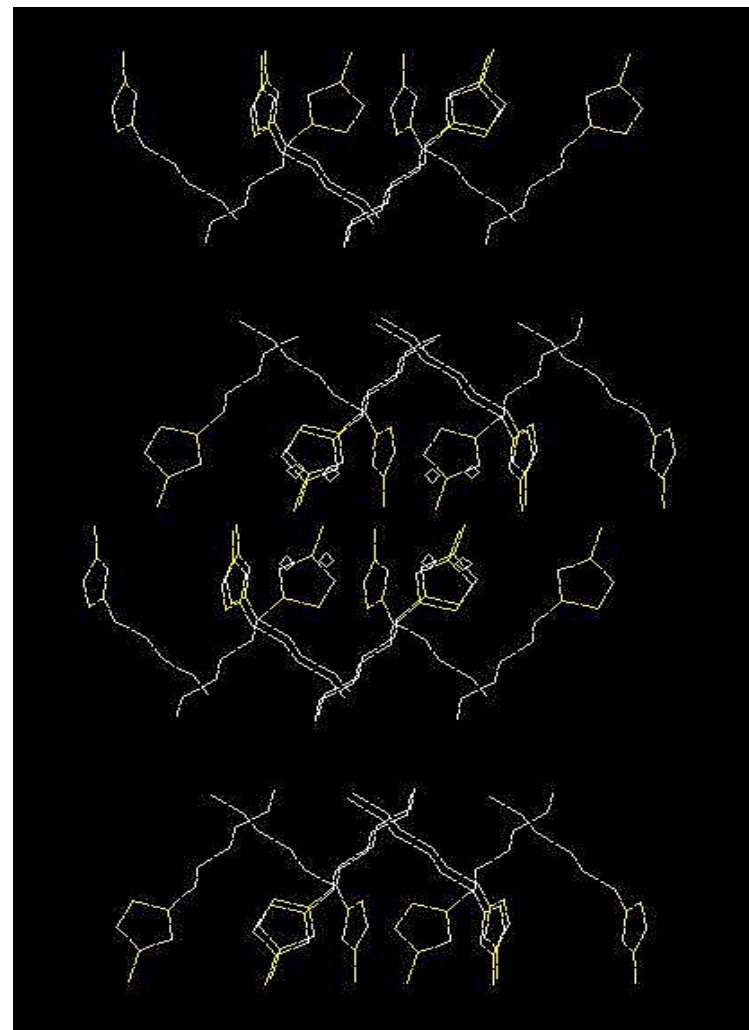
Packing view revealing significant cation-anion contacts in 1-n-propyl-4-amino-1,2,4-triazolium bromide.



Structure of Ionic Liquids



1-dodecyl-3-methylimidazolium hexafluorophosphate⁹

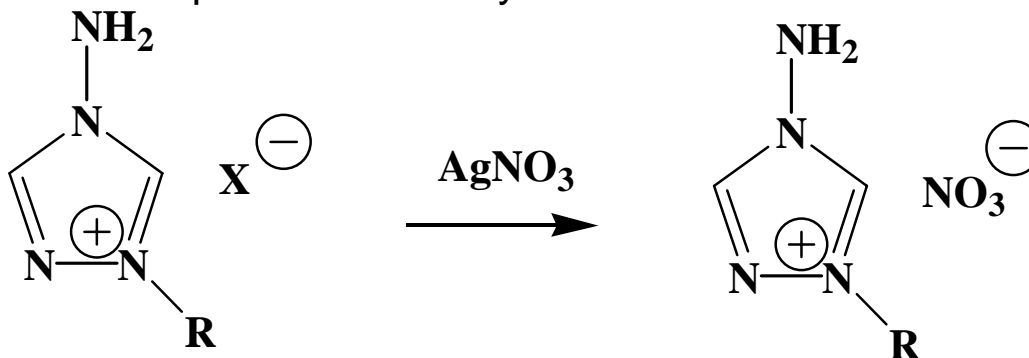


1-hexyl-4-amino-1,2,4-triazolium bromide⁸



Synthesis of 1-R-4AT Nitrate Ionic Liquids

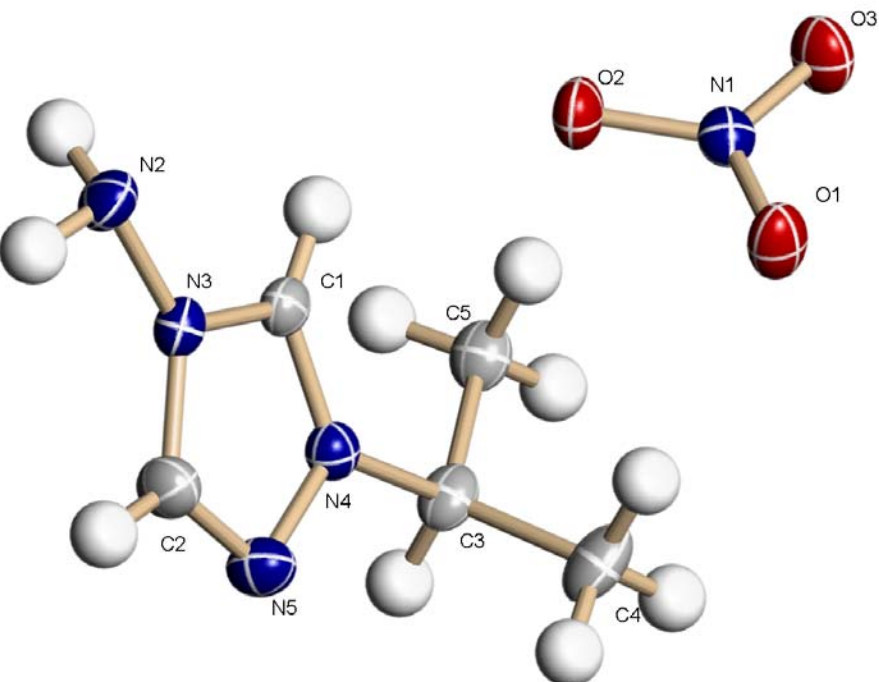
Metatheses of the corresponding halide salts with silver nitrate resulted in the desired nitrate ionic liquids in high yields and purities with easy isolation.⁸



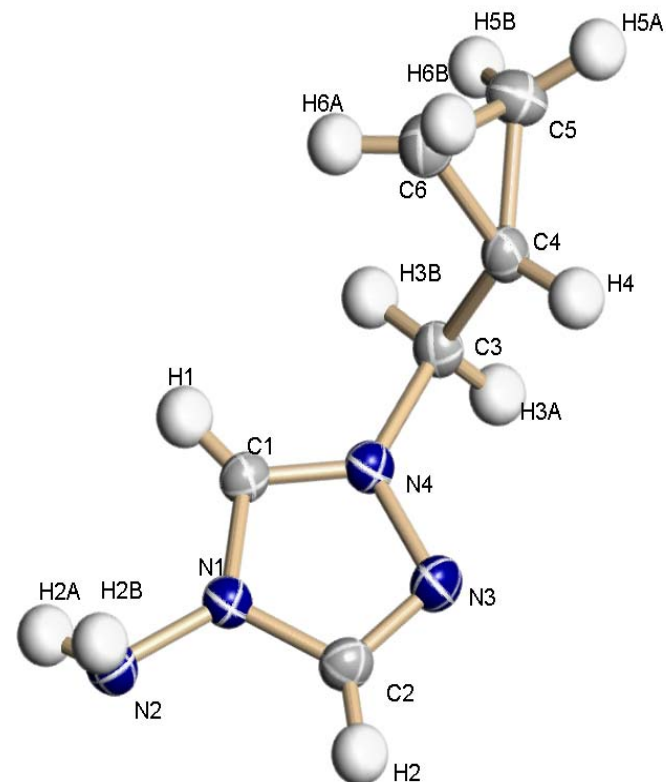
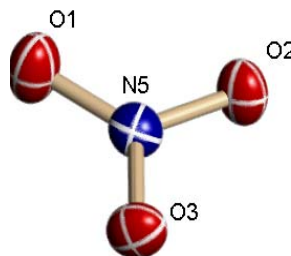
Salt	melting point($^{\circ}\text{C}$)	decomp onset($^{\circ}\text{C}$)
1-methyl	-54(g)	175
1-ethyl	-55(g)	160
1-n-propyl	33	175
1-isopropyl	66	180
1-(2-propenyl)	-50(g)	140
1-n-butyl	-50 (g)	170
1-methylcyclopropyl	56	185
1-n-pentyl	29	180
1-n-hexyl	0	170
1-n-heptyl	35	165
1-n-octyl	34	165
1-n-nonyl	53	175
1-n-decyl	51	185



X-ray Diffraction Studies of Nitrate Ionic Liquids



1-isopropyl-4-amino-1,2,4-triazolium nitrate

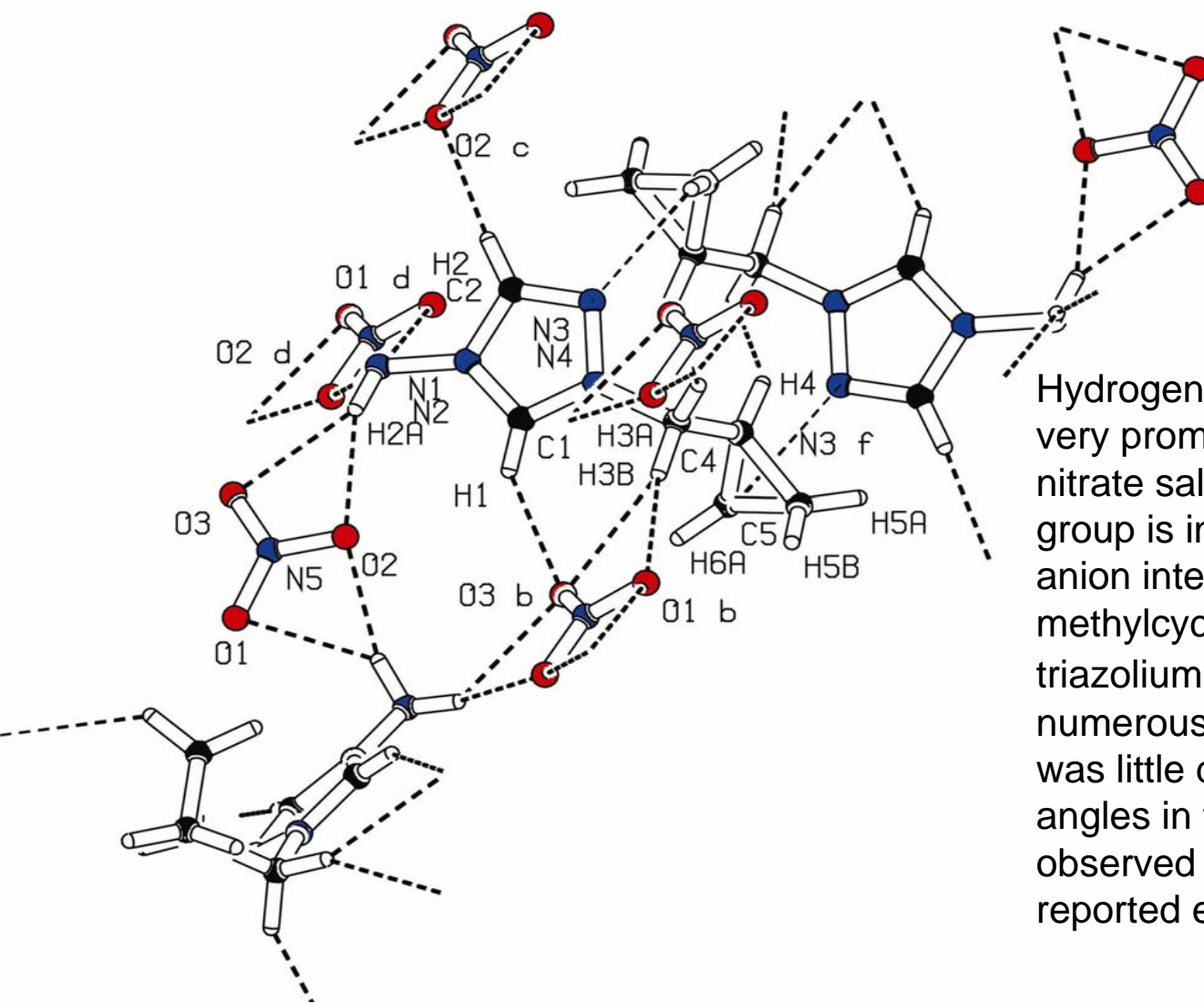


1-methylcyclopropyl-4-amino-1,2,4-triazolium nitrate

Single crystal x-ray studies verified the Structures of the new class of nitrate ionic liquids.⁸



X-ray Diffraction Studies of Nitrate Ionic Liquids

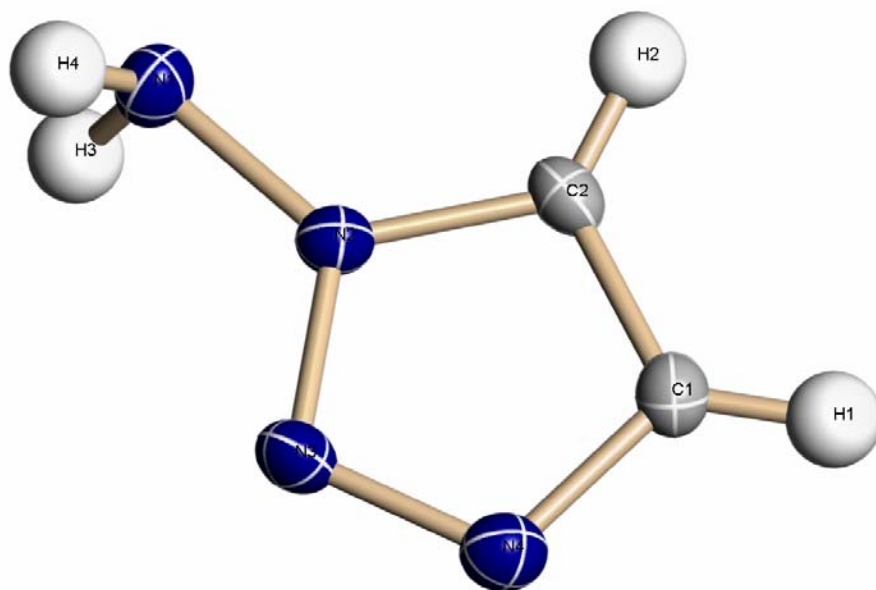
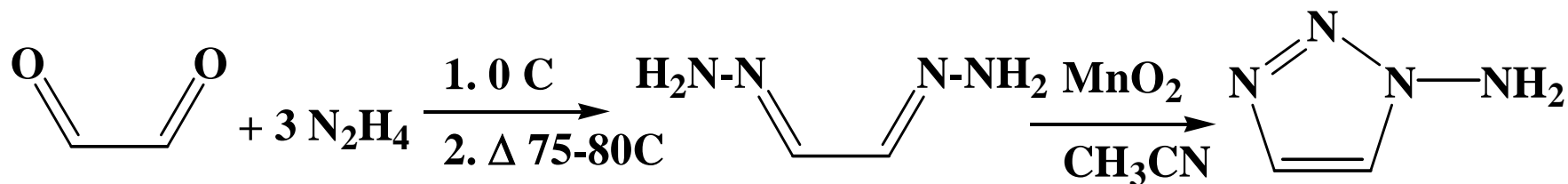


Hydrogen bonding was very prominent in the structure of the nitrate salts. The pendant N-amino group is involved in many cation-anion interactions in the structure of 1-methylcyclopropyl-4-amino-1,2,4-triazolium nitrate (left). Despite the numerous cation-anion contacts, there was little deviation in bond distances or angles in the cation from those observed in similar heterocyclic systems reported elsewhere.



Work with 1-Amino-1,2,3-Triazole

Investigations of the isomer of 4-amino-1,2,4-triazole have begun looking at 1-amino-1,2,3-triazole revealing a similar chemistry. 1-amino-1,2,3-triazole was made in a two step process using hydrazine and glyoxal forming the bishydrazine followed by oxidation with manganese dioxide forming 1-amino-1,2,3-triazole in good yields¹⁰.

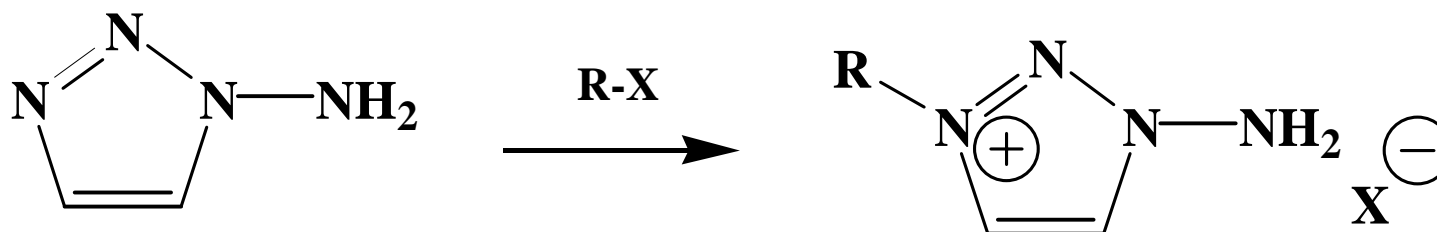


Single crystal x-ray diffraction studies verified the structure 1-amino-1,2,3-triazole (left).



Work with 1-Amino-1,2,3-Triazole

Using the same kind of alkylation conditions employed for alkylating 4-amino-1,2,4-triazole, 1-amino-1,2,3-triazole was easily alkylated at the N(3) position resulting in the desired quarternary salts in high yields and purities.¹⁰

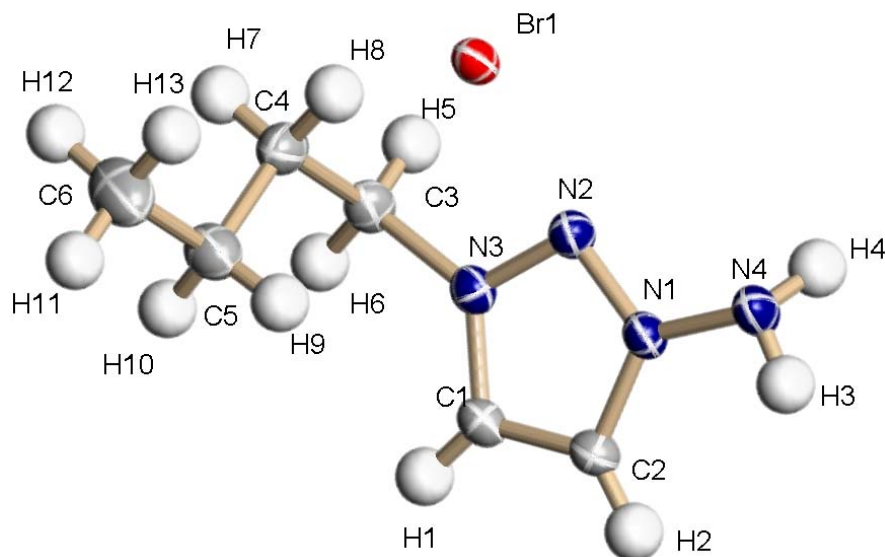


<u>3-R-1-amino salt</u>	<u>melting point(°C)</u>	<u>decomp onset(°C)</u>
3-methyl I ⁻	142	145
3-ethyl Br ⁻	115	165
3-n-propyl Br ⁻	126	155
3-n-butyl Br ⁻	129	150
3-allyl Br ⁻	96	140

Unlike their 1-alkyl-4-amino-1,2,4-triazolium halide analogues, the 1-amino-3-alkyl-1,2,3-triazolium halides are high melting and are not ionic liquids!



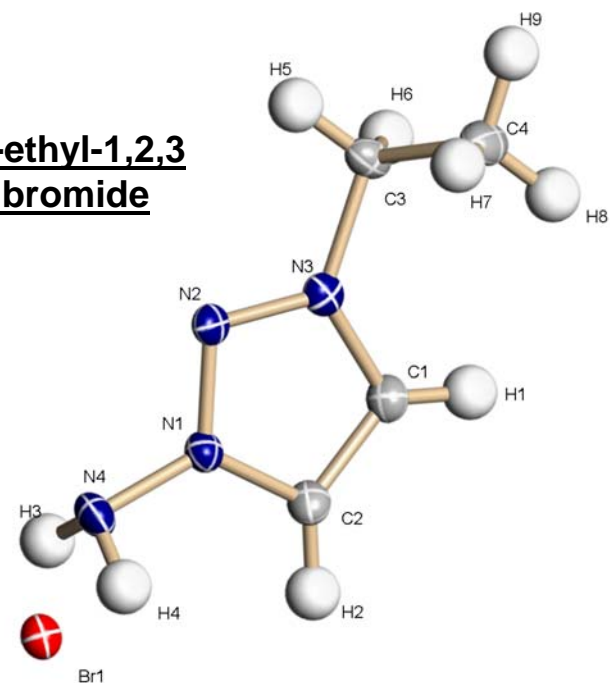
X-ray Studies of 1-Amino-3-Alkyl-1,2,3-Triazolium Salts



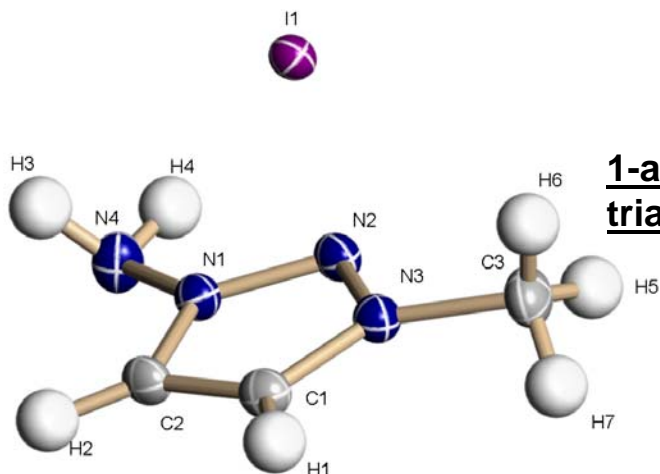
**1-amino-3-n-butyl-1,2,3
triazolium bromide**

Single crystal x-ray studies of several of the new quaternized heterocyclic salts verified their structures which, like their 4-amino-1,2,4-triazolium analogs, had extensive hydrogen bonding in the solid state.

**1-amino-3-ethyl-1,2,3
triazolium bromide**



**1-amino-3-methyl-1,2,3
triazolium iodide**

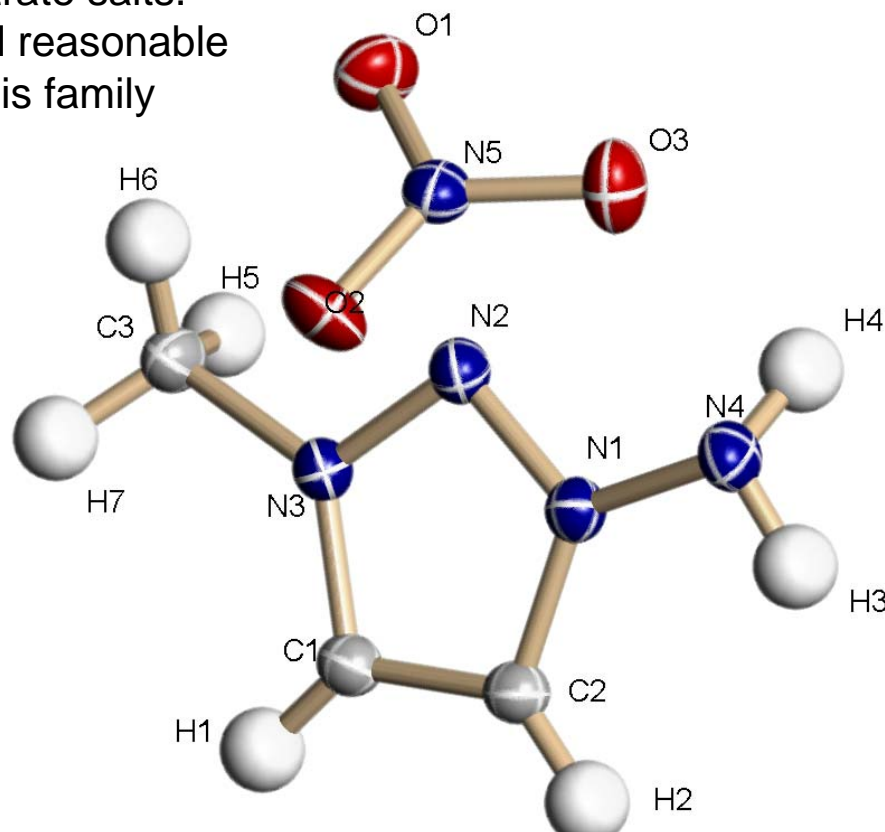




1-Amino-3-Alkyl-1,2,3-Triazolium Nitrate Ionic Liquids

Using simple metathesis with silver nitrate, the halide salts were converted in high yield and purity to the desired nitrate salts.¹¹ These new nitrate salts had low melting points and reasonable liquidous ranges before decomposition, defining this family of quaternized 1-amino-1,2,3-triazolium salts as a new class of ionic liquids!

<u>New ionic liquid</u>	<u>melting point</u>	<u>DSC onset</u>
1-amino-3-methyl-1,2,3-triazolium nitrate	86-88°C	185°C
1-amino-3-ethyl-1,2,3-triazolium nitrate	30-32°C	165°C
1-amino-3-propyl-1,2,3-triazolium nitrate	33-35°C	165°C
1-amino-3-(2-propenyl)-1,2,3-triazolium nitrate	8-11°C	135°C
1-amino-3-butyl-1,2,3-triazolium nitrate	48-50°C	175°C



X-ray structure of 1-amino-3-methyl-1,2,3-triazolium nitrate



Summary and Conclusions/ Acknowledgements



Summary and Conclusions

Two new classes of ionic liquids based upon N-alkylated triazoles using either 4-amino-1,2,4-triazole or 1-amino-1,2,3-triazole have been discovered. In the case of 4-amino-1,2,4-triazole, both the halide salts as well as the nitrate salts had melting points below 100°C defining them as new ionic liquids. Using 1-amino-1,2,3-triazole as a starting material, the quarternized halide salts had high melting points >100°C, yet their nitrate analogs had melting points well below 100°C defining them as a new class of ionic liquids as well. In both heterocyclic families, N-amino hydrogen bonding was very evident in the single crystal x-ray studies with many cation anion interactions. However, this had little effect upon the bond distances and angles in the heterocyclic cations in any of the structures. Investigations using other charge delocalized anions is underway with these alkylated heterocyclic systems.

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